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(54) Low temperature process for depositing oxide layers by photochemical vapor deposition.

(57) The specification discloses a low temperature process for depositing oxide layers on a substrate by photochemical vapor deposition, by exposing the substrate to a selected vapor phase reactant in the presence of photo-chemically generated neutral (un-ionized) oxygen atoms. The oxygen atoms react with the vapor phase reactant to form the desired oxide, which deposits as a layer on the substrate. The use of photochemically generated neutral oxygen atoms avoids damage to the substrate due to charge bombardment or radiation bombardment of the substrate. The deposited oxide layer may optionally incorporate a selected dopant material in order to modify the physical, electrical, or optical characteristics of the oxide layer.

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LOW TEMPERATURE PROCESS FOR
DEPOSITING OXIDE LAYERS BY
PHOTOCHEMICAL VAPOR DEPOSITION

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TECHNICAL FIELD

This invention relates generally to the manufacture of semiconductor devices and, more particularly, to a photochemical vapor deposition process for forming a dielectric oxide layer on the surface of a selected semiconductor material or an optical substrate, using a low temperature and non-ionizing radiation.

BACKGROUND ART

10 In the manufacture of semiconductor devices, it is frequently necessary to form a dielectric layer either as a passivation layer to permanently protect the surface of the substrate or as a mask during such procedures as etching, solid state diffusion, or ion-implantation.

15 One method by which an oxide layer, such as silicon dioxide (SiO_2), may be formed is a plasma-enhanced chemical vapor deposition process as described by James A. Amick, G. L. Schnable, and J. L. Vossen, in the publication entitled, "Deposition Techniques for Dielectric Films or Semiconductor Devices," in the Journal of Vacuum Science Technology, Vol. 14, No. 5, Sept.-Oct. 1977, pp. 1053-1063. In such a plasma-enhanced process, the vapor phase reactants, such as silane (SiH_4) and nitrous oxide (N_2O), are subjected to a radio frequency discharge, which creates an ionized plasma of the reactant gases. These ionized reactants then interact to form the desired reaction

1 product. However, as a result of the exposure of the
reactant gases to the radio frequency discharge, numerous
extraneous ionized and neutral particles, as well as high
energy radiation with wavelengths as low as 500 angstroms
5 (Å) and even extending into the x-ray region, are produced and bombard the surface of the substrate on which the oxide is being formed. If the substrate comprises a sensitive device type, such as a charge coupled device or a device formed of certain compound semiconductors
10 (e.g., InSb, HgCdTe, or GaAs), the above-described charged particles and unwanted radiation frequently impart damage to these sensitive devices. For example, the deposited oxide layer may incorporate charges or dangling bonds, which create high surface state densities (N_{ss}) at the
15 semiconductor device/oxide layer interface and which will trap charges when a voltage is applied to the device, thereby preventing optimum device performance. In addition, a plasma enhanced deposition process has the disadvantage that plasma-induced heating of the substrate
20 occurs as a result of selective absorption of the radio frequency energy by the substrate, and this heating causes uncertainty in the temperature of the substrate, which prevents optimization of the characteristics of the deposited oxide layer.

25 Other methods by which oxide layers may be formed use a non-reactive or a reactive sputtering technique. By a non-reactive sputtering technique, as described, for example, by Amick et al as referenced above, a disk of the selected oxide material, such as SiO_2 , is bombarded with argon ions, which cause the SiO_2 to vaporize,
30 and the vaporized SiO_2 subsequently deposits on the selected substrate. By a reactive sputtering technique, as described, for example, by Amick et al as referenced above, a disk of silicon is bombarded with oxygen ions, which
35 causes vaporization of the silicon, and the vaporized silicon and oxygen ions then react to produce the desired

1 SiO₂. However, these sputtering techniques are similar
to the above-described plasma processes in that they fre-
quently impart damage to sensitive devices due to charge
bombardment or radiation bombardment of the device. In
5 addition, the films produced by sputtering techniques
are often granular, not dense, and not specular (i.e.,
having good light reflecting properties).

Both the sputtering technique and the plasma-
enhanced method for chemical vapor deposition may be
10 used to deposit a dielectric layer which incorporates
a selected dopant material. In the former case, an
appropriately doped target could be bombarded by
selected ions. In the latter case, a dopant-containing
material is added to the reactant gases which are then
15 ionized. However, both the above sputtering technique
and the above plasma-enhanced method suffer from the
difficulties discussed above, particularly that of
imparting damage due to charge bombardment or radiation
bombardment and plasma-induced heating of the substrate.

20 Still another method by which oxide layers may be
formed involves thermal processes as described by
Amick et al as referenced above. In order to form SiO₂,
for example, by a thermal process, silane is brought
into contact with oxygen at a low temperature and a
25 spontaneous reaction occurs, forming SiO₂. The films
formed by thermal processes, however, are usually granu-
lar, do not necessarily have good adhesion, and tend
to incorporate traps.

It is the alleviation of the prior art problem
30 of imparting damage to sensitive devices due to charge
bombardment or radiation bombardment during the formation
of an oxide layer thereon to which the present invention
is directed.

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SUMMARY OF THE INVENTION

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The general purpose of this invention is to provide a new and improved process for depositing a layer of an oxide of a chosen material on the surface of a selected substrate by low-temperature photochemical vapor deposition. This process possesses most, if not all, of the advantages of the above prior art oxide deposition processes, while overcoming their above-mentioned significant disadvantages.

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The above general purpose of this invention is accomplished by exposing the substrate to a selected vapor phase reactant in the presence of photochemically generated, neutral (unionized) oxygen atoms. The oxygen atoms react with the vapor phase reactant to form the desired oxide, which deposits as a layer on the substrate. The use of photochemically generated neutral oxygen atoms avoids damage to the substrate due to charge bombardment or radiation bombardment.

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Accordingly, it is an object of the present invention to provide a new and improved process for depositing a layer of an oxide of a chosen material on the surface of a selected substrate by a novel, low-temperature chemical vapor deposition process which avoids damage to the substrate from charge- or radiation-bombardment.

30

Another object of the present invention is to provide a process of the type described which minimizes the value of the surface state density at the oxide/semiconductor substrate interface and thus minimizes the charge traps in the deposited oxide layer.

35

Still another object is to provide a process of the type described which produces a low density of generation/recombination centers in the deposited oxide layer, and thus provides good minority carrier lifetime and reduced susceptibility to radiation damage in the device formed by this process.

BAD ORIGINAL



1 Another object is to provide a process of the type
described which is performed at a temperature as low as
room temperature (e.g. 30°C) and thus eliminates the
problems of boundary migration and the resulting decreased
5 device yields which are encountered in the fabrication
of high density/high speed devices at higher temperatures.

Yet another object of the present invention is to
provide a process of the type described which produces
dense, non-granular, adherent oxide films on selected
10 substrates.

Another object of the present invention is to
provide a new and improved process for depositing a
layer of a chosen oxide containing a selected dopant
material on the surface of a substrate by a chemical
15 vapor deposition process which avoids damage to the sub-
strate due to charge bombardment or radiation bombardment.

Still another object is to provide a new and
improved process for depositing a layer of a chosen oxide
containing a selected dopant material on the surface
20 of a substrate, which uses a photochemical technique.

The foregoing and other objects, features, and
advantages of the present invention will be apparent
from the following more particular description of the
preferred embodiments of the invention, as illustrated
25 in the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates, in schematic form, a preferred
apparatus for carrying out the processes according to
30 first and second embodiments of the present invention,
in which neutral oxygen atoms are formed by the mercury
photosensitized dissociation of an oxygen-containing
precursor and are reacted to form an undoped or a doped
oxide layer, respectively.

35 FIG. 2 illustrates, in schematic form, a preferred
apparatus for carrying out the processes according to

1 third and fourth embodiments of the present invention,
in which neutral oxygen atoms are formed by the direct
dissociation of an oxygen-containing precursor and are
reacted to form an undoped or a doped oxide layer,
5 respectively.

DETAILED DESCRIPTION OF THE INVENTION

FIG. 1 shows, in simplified form, an apparatus suitable
for implementation of two process embodiments of the present
10 invention in which neutral oxygen atoms are formed by the
mercury photosensitized dissociation of a chemically
unreactive oxygen-containing precursor, such as nitrous
oxide (N_2O), molecular oxygen (O_2), or nitrogen dioxide
(NO_2). (The term "chemically unreactive" is used herein
15 to denote that a substance will not react with the
designated reactants under normal mixture conditions.)
A reaction chamber 10, in which the chemical vapor depo-
sition reaction occurs, is provided with a quartz window
12, which is integral with the top surface of the reaction
20 chamber 10. The quartz window 12 is transmissive to the
selected wavelength of radiation used to initiate the
desired photochemical reaction to be discussed below,
and this radiation 14 of a selected wavelength is produced
by the radiation-producing means 16, which may be, for
25 example, an array of low pressure mercury vapor arc lamps.
Within the reaction chamber 10, there is a substrate
holder 18, which receives a substrate 20 onto which the
desired oxide layer is to be deposited.

External to the reaction chamber 10 and adjacent to
30 the bottom surface thereof, there are heating elements
21, which may be formed, for example, of Nichrome wire
and are activated by applying a controlled voltage
thereto. The heating elements 21 may be used optionally
to heat the substrate 20 to the required temperature
35 so that appropriate properties of the deposited layer,
such as density, may be obtained. The temperature in

1 the chamber 10 may be maintained as low as room temper-
ature (i.e. 30°C) or as high as required (e.g., 300°C
or higher). However, since mercury vapor arc lamps, for
example, become less efficient at increased temperatures,
5 it is necessary to provide external water cooling or an
external air or nitrogen cooling source to cool these
lamps and remove radiant heat produced by the substrate 20
and substrate holder 18 at certain elevated temperatures
(as high as 600°C, for example, or higher). For this
10 purpose, the radiation-producing means 16 is completely
contained within the enclosure 23, which may be formed
of aluminum, and an external cooling means 25, such as
pipes with water flowing therethrough as shown in FIG. 1
or flowing nitrogen gas, is activated to apply cooling
15 to the enclosure 23. The enclosure 23 is secured to the
outside surface of the reaction chamber 10 which surrounds
the quartz window 12, but may be removed therefrom as
required. Thus, the processing temperature is maintained
at a level such that sufficient cooling of the mercury
20 lamps can be accomplished in order to provide efficient
lamp performance. The enclosure 23 also provides eye
protection to the operator from the radiation 14. Leading
from the reaction chamber 10, there is a tube 22 which
passes through a valve 24 and then to a vacuum-producing
25 means, such as a pump, (not shown), which is used to
evacuate the chamber 10 to a sufficiently low pressure
to allow the vapor deposition reaction to occur.

External to the reaction chamber 10, there are cham-
30 bers 26 and 28 which contain the individual reactant gases
for the selected chemical vapor deposition reaction, for
example, silane and nitrous oxide. The chambers 26 and
28 are connected to control valves or flowmeters 30 and
32, respectively, which are used to control the amounts
of reactants which are introduced into a tube 34. Alter-
35 natively, for a second process embodiment of the present
invention (discussed below), there are included a third

1 chamber 27, which contains the precursor of the selected
dopant material, such as phosphine, and a corresponding
control valve or flowmeter 31, which controls the amount
of dopant precursor introduced from the chamber 27 into
5 the tube 34, where it is mixed with the other reactant
gases discussed above.

The reactant gases flow through the tube 34 into a
chamber 36 which contains a pool of mercury (at room
temperature) having mercury vapor above it, at a vapor
10 pressure of 10^{-3} Torr at 30°C. The reactant gases thus
become mixed with mercury vapor in the chamber 36 and
this reactant gas mixture then passes through a tube 38
and into the reaction chamber 10, where the chemical vapor
deposition reaction may be brought about. The components
15 of the apparatus shown in FIG. 1 may be constructed of
stainless steel or aluminum, unless otherwise specified.
The apparatus shown in FIG. 1 may be used for either
a low pressure continuous flow photochemical reactor
system, in which there is a continuous influx of reactant
20 gases and removal of reaction by-products during the
photochemical reaction process, or for a static photo-
chemical reactor system, in which specified amounts of
reactants are introduced into the reaction chamber, the
flow of reactant gases is stopped, and then the photo-
25 chemical reaction process is allowed to occur.

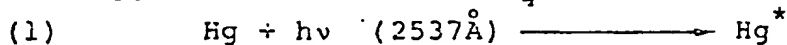
In practicing the present invention in accordance
with the first embodiment thereof, which depends on the
photochemical generation of atomic oxygen, and using the
apparatus of FIG. 1 with only two reactant gas chambers
30 (chambers 26 and 28), a chemical vapor deposition process
is performed as generally described by Werner Kern and
Richard S. Rosler in the publication entitled, "Advances
in Deposition Processes for Passivation Films", in the
Journal of Vacuum Science Technology, Vol. 14, No. 5,
35 Sept.-Oct. 1977, pp. 1082-1099, in the discussion of
low pressure chemical vapor deposition processes. The

1 reaction chamber 10 is evacuated by the vacuum-producing
means to a predetermined pressure, for example 1 to 4 Torr.
The selected vapor phase reactant, such as SiH_4 , is placed
in a chamber such as the chamber 26, and a chemically
5 unreactive oxygen-containing precursor, such as N_2O , is
placed in a chamber such as the chamber 28. The valves 30
and 32 are set so that the reactants from the chambers 26
and 28, respectively, in a predetermined ratio and at a
predetermined flow rate may pass into the tube 34 and then
10 into the chamber 36, which contains a pool of mercury.
These reactant gases become mixed with mercury vapor in the
chamber 36 and pass from the chamber 36 through the tube
38 into the reaction chamber 10, which is maintained at
approximately room temperature (e.g. 30°C) or up to 200°C
15 or higher. The radiation-producing means 16 is activated
and produces the radiation 14 of a selected wavelength
required to produce the desired photochemical reaction
(e.g. 2537\AA to produce mercury in an excited state). The
radiation 14 passes through the quartz window 12 into the
20 reaction chamber 10, where it excites the mercury (Hg)
atoms in the reactant gas mixture to form mercury atoms
in an excited state (Hg^*) (approximately 5 electron volts
above normal ground state, but unionized), as shown in
Equation (1) below. The Hg^* then collides with the oxygen-
25 containing precursor, such as N_2O , and causes the precursor
to dissociate and produce atomic oxygen (O), as shown in
Equation (2a) below.

In addition, the Hg^* may react with the selected
vapor phase reactant, such as SiH_4 , to produce a
30 reactive radical, such as $\cdot\text{SiH}_3$, as shown in equation
(2b) below. Finally, the atomic oxygen reacts with the
reactant, SiH_4 , or the reactive radical, such as $\cdot\text{SiH}_3$,
to produce the desired oxide, such as SiO and SiO_2 , as
shown in Equations (3a) and (3b) below. Either SiO or
35 SiO_2 can be produced, depending on the reactant gas ratio

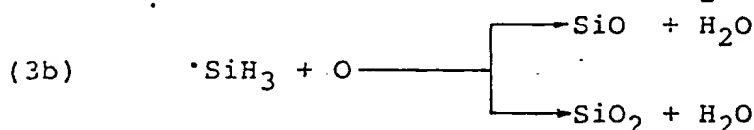
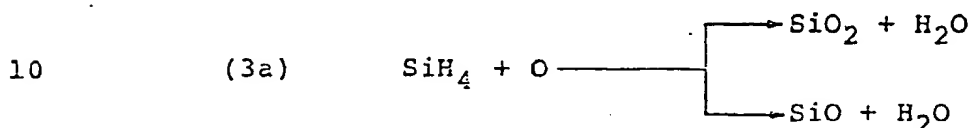
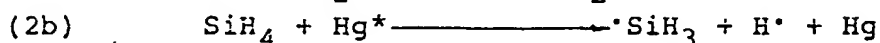
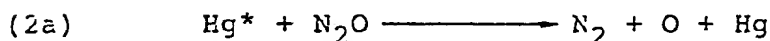


1 of SiH_4 and N_2O (i.e. the steady state concentration of atomic oxygen which oxidizes SiH_4).



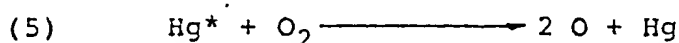
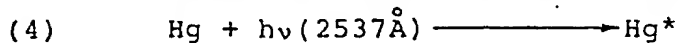
where h = Planck's constant

ν = frequency of absorbed radiation



15 The reaction of Hg^* with SiH_4 to form the radical $\cdot\text{SiH}_3$ is a side reaction which is not necessary to the process of the present invention, but leads to the same end product as the major reaction path. The atomic oxygen produced in Equation (2a) above may react directly with the selected vapor phase reactant without first forming an intermediate radical, as described in Equation (3a) above.

Alternatively, the atomic oxygen required for this first process embodiment of the present invention may be formed by the mercury sensitized dissociation of nitrogen dioxide (NO_2) to form atomic oxygen and NO . Further, atomic oxygen may also be formed by the mercury sensitized dissociation of molecular oxygen in accordance with Equations (4) and (5) below, or by other known means for forming atomic oxygen by photochemical processes.



Since molecular oxygen reacts spontaneously with SiH_4 as discussed in relation to the prior art thermal oxidation process, it is necessary to inhibit this spontaneous thermal oxidation process in order to permit

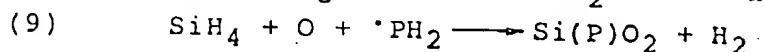
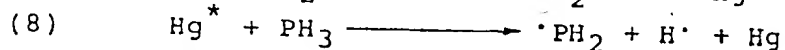
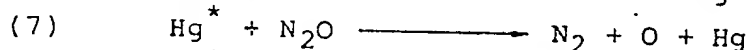
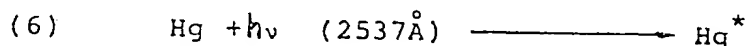
1 the formation of atomic oxygen and the reaction thereof
with SiH_4 in accordance with the process of the present
invention. This inhibition is accomplished by carefully
controlling the operating pressure and the ratio of
5 reactant gases, as discussed in more detail in Example 3
below. By controlling such process parameters the thermal
oxidation process may be completely inhibited and
the oxidation process of the present invention may occur
without any competing processes.

10 By the above-described process of the present
invention, oxygen atoms are produced by a photochemical
process which generates only neutral particles. Thus,
the prior art problems associated with the generation
of charged particles and high energy radiation which
15 bombard the substrate have been avoided. The value
of the surface state density (N_{ss}) at the oxide/semi-
conductor substrate interface and thus the charge
traps in the oxide or insulator layer are minimized by
the process of the present invention. In addition, a low
20 density of generation/recombination centers (i.e., dang-
ling bonds or traps) is produced and thus good minority
carrier lifetime is achieved in devices formed by the
process of the present invention. In addition, the
process of the present invention provides enhanced pro-
25 tection against device damage due to radiation (i.e.
from a cobalt-60 source) by minimizing the creation of
dangling bonds and traps during the deposition of the oxide
or insulator layer. These traps and dangling bonds nor-
mally increase the probability of radiation damage to
30 the device and their minimization thus ~~minimizes the~~ ^{reduces the probability of}
radiation damage. Further, the problem of boundary
migration has been eliminated since the process of the
present invention can be conducted at a relatively low
temperature, i.e. as low as room temperature, and the
35 associated problem of decreased device yield encountered
in the high temperature fabrication of high density

1 devices such as very large scale integrated circuits and
very high speed integrated circuits, has been avoided.
In addition, the prior art problem of plasma-induced
heating is avoided by the process of the present invention
5 since selective absorption of radiation by the substrate
does not occur in the process described herein. Further-
more, the process of the present invention is free of
particulate formation, for example, on chamber walls,
which is a problem often encountered in the prior art
10 processes discussed above. Finally, the oxide layer
formed by the process of the present invention is dense,
non-granular, scratch-resistant, specular, has negligible
porosity, and is strongly adherent to a variety of sur-
faces, such as semiconductor, metal and inorganic sur-
15 faces. Such oxide layers find utility both as a passi-
vation layer and as a gate insulator layer in integrated
circuit devices. Furthermore, these oxide layers may
be used as a conformal coating on integrated circuits
and hybrid microcircuits. In addition, these oxide
20 layers may be used in the fabrication of HgCdTe photo-
conductive and photovoltaic devices. This first process
embodiment of the present invention and the related third
process embodiment discussed below are, to my knowledge,
the first demonstration of the use of a photochemical
25 process for the deposition of a dielectric layer on a
substrate.

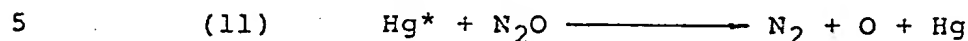
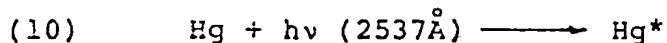
Using the above-described process, the present
invention may also be used to oxidize trimethyl aluminum,
(CH₃)₃ Al, to Al₂O₃; trimethyl gallium, (CH₃)₃ Ga, to
30 Ga₂O₃; germane, GeH₄, to GeO₂; diborane, B₂H₆, to B₂O₃;
trimethyl indium, (CH₃)₃ In to In₂O₃; titanium tetra-
chloride, TiCl₄, to TiO₂; tungsten hexafluoride, WF₆,
to W₂O₃, and hafnium hydride, HfH₄, to HfO₂. This first
process embodiment of the present invention is illustrated
35 in Example 1 below.

1 Furthermore, a process carried out in accordance
 with a second embodiment of the present invention may be
 performed by practicing the present invention as described
 above, using the apparatus of FIG. 1 with three (3)
 5 reactant gas chambers (chambers 26, 27, and 28), to deposit
 on the surface of a chosen substrate an oxide layer which
 incorporates a selected dopant material in order to
 modify the physical, electrical, or optical character-
 10 istics of the oxide layer. To accomplish this second
 process embodiment of the present invention, the selected
 vapor phase reactant, such as SiH_4 , is exposed to simul-
 taneously formed and photochemically generated neutral
 oxygen atoms and neutral atoms or atomic fragments of
 15 the selected dopant, such as phosphorus - containing
 phosphinyl radicals. The neutral atomic particles are
 produced by the mercury photosensitized dissociation
 of a chemically unreactive oxygen-containing precursor,
 such as nitrous oxide (N_2O) and a chemically unreactive
 20 dopant-containing precursor, such as phosphine (PH_3),
 which results in the generation of atomic oxygen and
 neutral phosphinyl radicals, respectively, as shown
 in Equations (6) through (8) below. The atomic oxygen
 and phosphinyl radicals subsequently oxidize the SiH_4
 to phosphorus-doped silicon dioxide [Si(P)O_2], as
 25 shown in Equation (9) below.



30 A mechanistic alternative to the sequence described
 above involves the simultaneous oxidation of both SiH_4 and
 PH_3 by atomic oxygen, as indicated in Equations (10)
 through (12) below. Thus, atomic oxygen alone may be suf-
 ficient to bring about the desired reaction as shown in
 35 Equation (12) below. Consequently, the production of neu-
 tral particles of the selected dopant material as described

1 above in Equation (8) may not be necessary in practicing
the second process embodiment of this invention, but
may occur.



The procedure followed to accomplish this second
process embodiment of the invention is essentially as
described above with respect to the first process embodi-
10 ment of the present invention, except that additionally,
a controlled amount of a selected dopant-containing pre-
cursor is introduced from the chamber 27 through the
control valve 31 into the tube 34, where it mixes with
the reactant gases from the chambers 26 and 28.

15 Thus, by this second process embodiment of the pre-
sent invention, a doped dielectric film may be deposited
by a low-temperature process which avoids the generation
of charged particles and high energy radiation and their
consequent bombardment damage to the substrate. Addition-
20 ally, this embodiment has all the advantages enumerated
above with respect to the formation of an undoped
dielectric layer by the process of the present invention.
This second process embodiment of the present invention
and the related fourth process embodiment discussed below
25 are, to my knowledge, the first demonstration of the
use of a photochemical process for the deposition of
a doped dielectric layer.

By the process according to this second embodiment
of the present invention, other dopants besides phosphorus
30 may be incorporated in the deposited dielectric layer by
addition of the corresponding dopant-containing precursor
to the reactant gas mixture. For example, diborane (B_2H_6)
may be used for boron doping, arsine (AsH_3) may be used for
arsenic doping, stibine (SbH_3) may be used for antimony
35 doping, hydrogen selenide (H_2Se) may be used for selenium
doping, hydrogen sulfide (H_2S) may be used for sulfur

1 doping, or hydrogen telluride (H_2Te) may be used for
tellurium doping. Other dopant-containing precursors
which are capable of the mercury photosensitized
dissociation reaction of the type discussed herein may
5 also be used. Other dielectric films besides SiO_2 may
be formed, as discussed above. This second process embodi-
ment of the present invention is illustrated in more
detail in Example 2 below.

Turning now to FIG. 2, there is shown an apparatus
10 suitable for implementation of the processes according to
of third and fourth embodiments of the present invention,
in which neutral oxygen atoms are formed by a direct
photochemical reaction of an oxygen-containing precursor,
thus eliminating the requirement of mercury photosensitiza-
15 tion. A reaction chamber 40 in which the photochemical
vapor deposition reaction occurs is provided with a trans-
parent window 42, which is integral with the top surface
of the chamber 40. The material of which the window 42
is formed is chosen to be transparent to the selected
20 wavelength of radiation which will be used for the photo-
chemical reaction. Radiation 44 having a selected
wavelength is produced by a radiation-producing means
46, such as an array of low pressure mercury vapor arc
lamps, and passes through the window 42 into the chamber
25 40. Within the reaction chamber 40, there is a substrate
holder 48, which holds a substrate 50 onto which the
desired oxide layer is to be deposited. External to the
reaction chamber 40 at the bottom surface thereof, there
are heating elements 51, which may be formed of Nichrome
30 wire and are activated by application of a controlled
voltage thereto. The heating elements 51 may be used
optionally to preheat the substrate 50 to the required
temperature for forming a deposited layer with desired
properties.



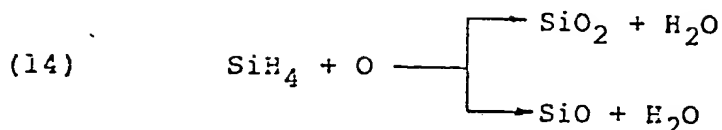
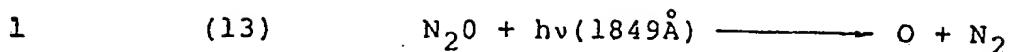
1 In practicing the present invention, the temperature
in the chamber 40 may be maintained as low as room tempera-
ture or as high as 200°C or higher. In order to provide
the required cooling of the radiation-producing means 46,
5 as previously discussed in relation to FIG. 1, radiation-
producing means 46 is completely enclosed within the
enclosure 53, which may be formed of aluminum, and an
external cooling means 55, such as pipes with water flow-
ing therethrough as shown in FIG. 2 or flowing nitrogen
10 gas, is activated to apply cooling to the enclosure 53.
The enclosure 53 performs the additional function of
eliminating the formation of ozone which would occur if
the radiation 44 (such as 1849 Å radiation) were allowed
to contact molecular oxygen in the open atmosphere,
15 which would cause the formation of atomic oxygen that
would then react with additional molecular oxygen in
the atmosphere to form ozone. The enclosure 53 is
secured to the outside surface of the reaction chamber
40 which surrounds the quartz window 42, but may be
20 removed therefrom as required.

 Leading from the reaction chamber 40, there is a
tube 52 which passes through a valve 54 and then to a
vacuum producing means, e.g., a vacuum pump, (not shown)
which is used to evacuate the chamber 40 to a sufficiently
25 low pressure (e.g., 1-4 Torr) to allow the vapor deposition
reaction to occur.

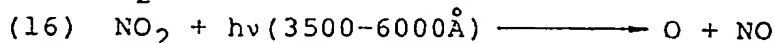
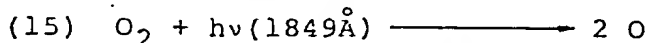
 External to the reaction chamber 40, there are
chambers 56 and 58, which contain the individual selected
reactant gases, such as silane (SiH_4) and nitrous oxide
30 (N_2O), respectively, for producing the desired photo-
chemical reaction. The chambers 56 and 58 are connected
to control valves or flowmeters 60 and 62, respectively,
which are used to control the amounts of reactants which
are introduced into a tube 64. Alternatively, in accord-
35 ance with a fourth process embodiment of the present
invention (discussed below), there are included a third

1 chamber 57, which contains the precursor of the selected
dopant material, such as phosphine, and a corresponding
control valve or flowmeter 61, which controls the amount
5 of dopant precursor introduced from the chamber 57 into
the tube 64, where it is mixed with the other reactant
gases discussed above. The reactant gases flow through
the tube 64 into the reaction chamber 40, where the
photochemical reaction may be brought about. The compo-
nents of the apparatus shown in FIG. 2 may be constructed
10 of stainless steel or aluminum, unless otherwise speci-
fied. The apparatus shown in FIG. 2 may be used for
either a continuous flow photochemical reactor system
or a static photochemical reactor system, as discussed
above with reference to FIG. 1.

15 In practicing the present invention in accordance
with the third embodiment thereof and using the apparatus
of FIG. 2, the general process described in relation
to the first process embodiment of FIG. 1 is followed,
except that no mercury is used for photosensitization.
20 The valves 60 and 62 are set so that the reactant gases,
such as SiH_4 and N_2O , from the chambers 56 and 58,
respectively, pass in a predetermined ratio and at a
predetermined flow rate into the tube 64 and then into
the reaction chamber 40. The radiation-producing means 46
25 is activated and produces the radiation 44 of a selected
wavelength, which is the appropriate wavelength to cause
the direct dissociation of the selected oxygen-containing
precursor (e.g. 1750-1950 \AA for N_2O). The radiation 44
passes through the window 42, which is formed of a mate-
30 rial that is transparent to the wavelength of the radia-
tion 44. The radiation 44 passes into the reaction cham-
ber 40, where it causes the dissociation of the selected
oxygen-containing precursor, such as N_2O , into atomic
oxygen, which then reacts with the selected vapor phase
35 reactant, such as SiH_4 , to form the desired oxide, such as
 SiO_2 and SiO , as shown in Equations (13) and (14) below.



5 Alternatively, the atomic oxygen required for this
third process embodiment of the present invention may
be formed by the direct photochemical dissociation of
molecular oxygen as shown in Equation (15) below or of
nitrogen dioxide (NO_2) as shown in Equation (16) below
10 or of similar known materials which are capable of
dissociation to oxygen by a direct photochemical process.



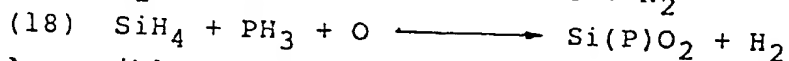
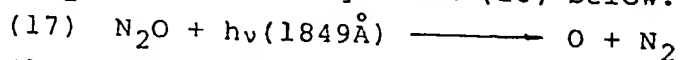
When molecular oxygen is used as the source of atomic
15 oxygen, the operating pressure and reactant gas ratio
must be carefully controlled in order to inhibit the
spontaneous thermal oxidation of the SiH_4 by the O_2 ,
as previously discussed in relation to an alternative
process embodiment of the present invention and as
20 illustrated in Example 3 below.

By the above-described process in accordance with
this third embodiment of the present invention, oxygen
atoms are generated by a photochemical process which
produces only neutral particles. Thus, the previously
25 discussed prior art problems caused by the generation
of charged particles and high energy radiation and their
bombardment of the substrate have been avoided. The
advantages of this third process embodiment of the present
invention are the same as those discussed in relation
30 to the first process embodiment described with respect
to FIG. 1. In addition, the process according to this
third embodiment has the advantage that no photosensitizing
mercury is necessary, and thus possible mercury contami-
nation of the deposited oxide can be avoided. Further,
35 the apparatus for carrying out the process according

1 to this third embodiment is less complex than an apparatus
requiring the use of mercury.

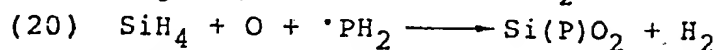
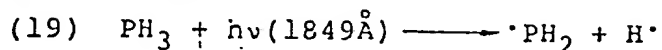
Using the above-described process, the present
invention may also be used to deposit dielectric oxides
5 of gallium, germanium, boron, and indium and metal oxides
of aluminum, tungsten, titanium, and hafnium, using the
gas phase reactants discussed in relation to FIG. 1.
This third process embodiment of the present invention
is illustrated in Example 3 below.

10 Furthermore, a process carried out in accordance
with a fourth embodiment of the present invention may
be performed by practicing the present invention as
described above, but also using the apparatus of FIG. 2
with three (3) reactant gas chambers (chambers 56, 57,
15 and 58), to deposit an oxide layer which incorporates
a selected dopant material, on the surface of a chosen
substrate. To accomplish this fourth process embodi-
ment of the present invention, the selected vapor phase
reactant, such as SiH_4 , is exposed to photochemically
20 generated neutral oxygen atoms in the presence of a
dopant-containing precursor, such as phosphine (PH_3).
The neutral atomic oxygen is produced by direct dissocia-
tion of an oxygen-containing precursor, such as N_2O ,
by radiation of a selected wavelength as shown in Equa-
25 tion (17) below. The atomic oxygen then simultaneously
oxidizes the SiH_4 and PH_3 to form the desired phosphorus-
doped SiO_2 as shown in Equation (18) below.



30 A possible alternative to the above-described
sequence involves the direct dissociation of the dopant-
containing precursor such as phosphine to form a neutral
phosphinyl radical as shown in Equation (19) below. The
phosphinyl radical so formed and the atomic oxygen formed
35 in accordance with the direct dissociation reaction of
Equation (17) above then react with the silane reactant :

1 to form the desired phosphorus-doped SiO_2 as shown in
Equation (20) below.



5 The procedure followed to accomplish the process
according to the fourth embodiment of this invention
is essentially as described above with respect to the
third process embodiment of the present invention, except
that additionally a controlled amount of a selected
10 dopant-containing precursor, such as phosphine gas, is
introduced from the chamber 57 and through the valve 61
into the tube 64, where it mixes with the reactant gases
from the chambers 56 and 58.

Thus, by this fourth process embodiment of the
15 present invention, a doped dielectric film may be
deposited by a low-temperature process which avoids
the generation of charged particles and high energy radia-
tion and their consequent bombardment damage to the
substrate and additionally avoids the use of mercury
20 for photosensitization. The significance of these
advantages has been discussed above with respect to
the third process embodiment of the present invention.
Various dopant materials other than phosphine may be
used, and these materials include diborane, arsine,
25 stibine, hydrogen selenide, hydrogen sulfide, hydrogen
telluride, or other dopant-containing precursors which
are capable of simultaneous oxidation by atomic oxygen
with the selected gas phase reactant to form the desired
doped oxide layer. This fourth process embodiment of
30 the present invention is illustrated in Example 4 below.

EXAMPLE 1

This example illustrates the use of the process
according to the first embodiment of the present inven-
35 tion as previously described herein.

1 Using the apparatus described and illustrated in
relation to FIG. 1 with two reactant gas chambers, SiO
and SiO₂ were independently deposited on the surface
of a wafer of silicon having a two-inch diameter. Nitrous
5 oxide was used as the oxygen-containing precursor and
silane was the selected vapor phase reactant. The reac-
tion chamber 10 was evacuated by the vacuum-producing
means to a pressure of 10⁻³ Torr, then back-filled with
nitrogen, and again evacuated to a pressure of 10⁻³ Torr.
10 The flowmeters 30 and 32 were activated to admit the
reactant gases (SiH₄ and N₂O) in a predetermined ratio
into the tube 34 and subsequently into the chamber 36
and the reaction chamber 10, and the reactant gas flow
rates were stabilized. The operating pressure within the
15 reaction chamber 10 was adjusted by means of the valve 24
to achieve a pressure of approximately 1 Torr. The heat-
ing elements 21 and the cooling means 25 were activated.
Finally, the low pressure mercury arc resonance lamps
were activated and emitted radiation at 2537Å, which
20 was absorbed by the mercury vapor in the reaction
chamber, producing photo-excited mercury atoms, which
collided with the nitrous oxide to form atomic oxygen.
The atomic oxygen then oxidized the silane to either
SiO₂ or SiO. When using a continuous flow photochemical
25 reactor system at an operating pressure of 2 Torr, with
a reactant gas flow ratio of 2 standard cubic centimeters
per minute (sccm) of SiH₄ to 50 sccm of N₂O, a layer of
SiO₂ was produced. When a reactant gas flow ratio of
2 sccm of SiH₄ to 10 sccm of N₂O was used in a continuous
30 flow system, a layer of SiO was produced. At a substrate
temperature of 100°C, the silicon oxide layer was deposi-
ted at the rate of 200Å per minute using a continuous
flow system. When using a static photochemical reactor
system with a reactant gas ratio of SiH₄ to N₂O of 3
35 millimeters (mm) to 12 mm, silicon monoxide (SiO) was
produced as a layer on the surface of the silicon wafer.

- 1 When a reactant gas ratio of SiH_4 to N_2O of 3.0mm to 30mm
was used in a static system, silicon dioxide (SiO_2)
was produced as the layer on the silicon wafer.

5 The refractive index of the photodeposited silicon
oxide layers formed by the process of this embodiment of
the present invention was determined by ellipsometry
as a function of the reactant gas mixture ratio, $\text{N}_2\text{O}/\text{SiH}_4$.
Mixtures rich in N_2O (i.e. atomic oxygen) produced
10 films with a refractive index characteristic of SiO_2 ,
i.e. 1.45. Mixtures of $\text{N}_2\text{O}/\text{SiH}_4$ progressively leaner
in N_2O yielded silicon oxide films with less oxygen
content and, ultimately, SiO with a refractive index
of 1.88. The etch rate characteristics of the photo-
deposited SiO_2 material in buffered HF were comparable
15 to those of SiO_2 films deposited by low temperature plasma
techniques. The stoichiometric composition of the film
was determined by Auger electron spectroscopy. The SiO_2
films exhibited an excellent composition/depth pro-
file and stoichiometrically were equivalent to pure
20 SiO_2 . The SiO films exhibited slower etch rates than
the SiO_2 films due to the depleted oxygen content of
the SiO films, which was confirmed by Auger spectroscopic
analysis. The breakdown voltage of the SiO_2 films formed
by the process of the present invention was determined
25 to be 3.0×10^6 volts/centimeter, the dielectric constant
was approximately 5.5, and the dissipation factor was
 1.5×10^{-2} , which measurements are comparable to the
values obtained for similar films formed by a prior art
thermal process previously discussed. The density of
30 the SiO_2 films formed by the process of the present
invention was 2.3 grams/cubic centimeter.

The photochemically deposited SiO_2 layers formed
by the above-described process of the present invention
have application as dielectric layers for the passivation
35 of semiconductor devices, particularly charge-sensitive
microelectronic devices, such as silicon MOS devices,



1 HgCdTe photoconductive and photovoltaic devices, and
GaAs field-effect transistors. These layers may be
deposited to a typical thickness of 1200-1500 \AA for such
a purpose. In addition, the process of the present inven-
5 tion may be used to deposit an anti-reflective oxide
coating on a lens, including a plastic lens, or a solar
cell, or to deposit a protective oxide coating on a mirror.

Using the above-described process, SiO_2 layers
were similarly deposited on Ge, InSb, and Al substrates.

10

EXAMPLE 2

This example illustrates the use of the process
according to the second embodiment of the present
invention as previously described herein.

15 Using the apparatus described and illustrated in
relation to FIG. 1 with three reactant gas chambers, a
layer of phosphorus-doped SiO_2 was deposited on the sur-
face of a silicon wafer having a two-inch diameter. The
general procedure described in relation to Example 1
20 above was followed, with the addition of a third reactant
gas. Nitrous oxide was used as the oxygen-containing
precursor, silane was the selected vapor phase reactant,
and phosphine was the phosphorus dopant-containing pre-
cursor. The process was initiated by the photochemical
25 excitation of mercury vapor at 10^{-3} Torr in a quartz
reaction chamber. Low pressure mercury arc resonance
lamps emitted radiation at 2537 \AA , which was absorbed
by the mercury vapor in the reaction chamber, producing
photo-excited mercury atoms that reacted with the N_2O
30 and PH_3 as shown in Equations (7) and (8) discussed above.
The atomic oxygen and neutral phosphinyl radical ($\cdot\text{PH}_2$)
thus formed reacted with the SiH_4 to form phosphorus-
doped silicon dioxide $[\text{Si}(\text{P})\text{O}_2]$ as shown in Equation
(9) discussed above, which deposited as a layer on the
35 silicon wafer. Using a continuous flow photochemical
reactor system, with a reactant gas flow ratio of



1 $\text{SiH}_4/\text{N}_2\text{O}/\text{PH}_3$ of 2/60/1 sccm, a phosphorus-doped SiO_2 layer was deposited on the substrate at the rate of 200Å/minute and the phosphorus content of the deposited
5 static photochemical reactor system was used with a reactant gas ratio of $\text{SiH}_4/\text{N}_2\text{O}/\text{PH}_3$ of 3/30/1 mm. The phosphorus-doped SiO_2 layer was deposited at initial rates of 200Å/minute and the phosphorus-content in the deposited layer was approximately 5%. Using a reactant
10 gas ratio of $\text{SiH}_4/\text{N}_2\text{O}/\text{PH}_3$ of 2/30/12 mm in a static system, levels of phosphorus-doping of 17% in the deposited layer have been achieved.

The refractive index of the photodeposited phosphorus-doped SiO_2 layer was dependent on the $\text{N}_2\text{O}/\text{PH}_3$
15 ratio and indices from 1.55 to 1.65 were measured. The films exhibiting the higher refractive indices indicated a greater phosphorus doping content of the SiO_2 dielectric material. The chemical composition of the phosphorus-doped SiO_2 films was determined by Auger electron spectroscopy and the phosphorus content was confirmed by energy
20 dispersive X-ray analysis (EDAX). The etch rate in "P-etch" [i.e., a mixture of 60 milliliters (ml) of water, 3 ml of 49% HF, and 2 ml of 70% HNO_3] of the phosphorus-doped SiO_2 films was significantly faster than that of
25 pure SiO_2 , yielding values of 200Å/second, which concur with values of phosphorus-doped films produced by known chemical vapor deposition techniques previously discussed. The amount of dopant contained in the dielectric layer deposited by the above-described process may be
30 controlled by adjusting the amount of dopant-containing precursor which is added to the reactant gas mixture.

Although phosphorus-doped SiO_2 layers were formed as described above, it is also possible to form phosphorus-doped SiO layers by this process embodiment
35 of the present invention by increasing the ratio of SiH_4 to N_2O in a manner similar to that described in Example 1.

1 The photochemically deposited phosphorus-doped
SiO₂ films formed by the above-described process of the
present invention have application as dielectric layers
for the passivation of charge-sensitive microelectronic
5 devices, such as silicon MOS devices. In addition, these
phosphorus-doped films may be used as a counter-diffusion
layer on GaAs devices for the minimization of out-
diffusion of both gallium (Ga) and arsenic (As) at tempera-
tures exceeding 100°C.

10 EXAMPLE 3

This example illustrates the use of the process
in accordance with the third embodiment of the present
invention as previously described herein.

15 Using the apparatus shown in FIG. 2 with two
reactant gas chambers, a layer of SiO₂ was deposited on
the surface of a wafer of silicon having a two-inch
diameter. The general procedure described in relation
to Example 1 above was followed, except that mercury
20 sensitization was not used. A continuous flow photo-
chemical reactor system was used. The oxygen-containing
precursor was N₂O and the selected vapor phase reactant
was SiH₄. Radiation having a wavelength of 1849Å
was used to dissociate the N₂O; and the window of the
25 reaction chamber was formed of "spectrasil" (obtained
from Thermal American Fused Quartz, Montville, New
Jersey), which was transparent to 1849Å radiation. Low
pressure mercury arc lamps designed with "spectrasil" en-
velopes emitted radiation at 1849Å, which was transmitted
30 through the "spectrasil" window into the reaction chamber.
The radiation was absorbed by the N₂O and caused dissocia-
tion thereof to produce atomic oxygen. The atomic oxygen
then reacted with the SiH₄ to produce the desired SiO₂
which deposited as a layer on the silicon wafer. A
35 reactant gas flow ratio of SiH₄ to N₂O of 2 sccm to 60
sccm and an operating pressure of 3.7 Torr were used. The

1 SiO_2 layer was deposited at the rate of 700\AA in 30 minutes, and even higher rates may be achieved with process optimization.

5 The refractive index of the photodeposited SiO_2 layer formed by the above-described process of the present invention was determined by ellipsometry and the films were found to have a refractive index characteristic of SiO_2 , i.e. 1.45. The etch rate characteristics of the photodeposited SiO_2 material in
10 buffered HF were comparable to those of SiO_2 films deposited by low temperature plasma techniques.

 Although SiO_2 layers were formed as described above, it is also possible to form SiO layers by this process embodiment of the present invention by increasing
15 the ratio of SiH_4 to N_2O in a manner similar to that described in Example 1.

 The photochemically deposited SiO_2 layers formed by the above-described process of the present invention have application as dielectric layers for the passivation
20 of semiconductor devices, particularly charge sensitive microelectronic devices, such as MOS devices and GaAs, HgCdTe photoconductive and photovoltaic devices, field-effect transistors. In addition, the oxide layers formed by the above-described process may be used on electro-
25 optical materials such as lenses and mirrors or on solar cells as described in relation to Example 1.

 Using the above-described process, SiO_2 layers were similarly deposited on Ge, InSb, and Al substrates.

 Furthermore, using the general process described
30 above, a layer of SiO_2 was deposited on the surface of a silicon wafer, using molecular oxygen (O_2) as the oxygen-containing precursor. In order to completely inhibit the spontaneous thermal oxidation reaction of O_2 and SiH_4 , a nitrogen gas diluent was used and the pressure
35 and flow rate conditions of the reactant gases were carefully controlled. Using an operating pressure of 0-5 Torr

- 1 and a reactant gas flow ratio of $\text{SiH}_4/\text{O}_2/\text{N}_2$ of 1/20/80
sccm, a layer of SiO_2 was deposited at the rate of 3000
to 4000 Å in 30 minutes. Thus, it may be seen that the
use of molecular oxygen as the oxygen-containing precursor
5 in practicing the present invention greatly enhances the
oxide deposition rate.

EXAMPLE 4

- 10 This example illustrates the use of the process
in accordance with the fourth embodiment of the present
invention as previously described herein.

- Using the apparatus described and illustrated in
relation to FIG. 2 with three reactant gas chambers, a
phosphorus-doped SiO_2 layer was deposited on the surface
15 of a silicon wafer having a two-inch diameter. The gene-
ral procedure described in relation to Example 3 above
was followed, with the addition of a third reactant gas.
A continuous flow photochemical reactor system was used.
Nitrous oxide was used as the oxygen-containing precursor,
20 silane was the selected vapor phase reactant, and phos-
phine was the dopant-containing precursor. Radiation
having a wavelength of 1849 Å was used to dissociate
the N_2O and the window of the reaction chamber was formed
of "spectrasil" as discussed in relation to Example 3.
25 The 1849 Å radiation was absorbed by the N_2O and caused
dissociation thereof to produce atomic oxygen. The atomic
oxygen then reacted with the SiH_4 and PH_3 as shown in
Equation (18) above, to produce the desired phosphorus-
doped SiO_2 , which deposited as a layer on the silicon
30 wafer. A low pressure continuous flow photochemical
reactor system was used with a reactant gas flow ratio of
 $\text{SiH}_4/\text{N}_2\text{O}/\text{PH}_3$ of 2/60/4 sccm. The SiO_2 was deposited at
the rate of 330 Å in 30 minutes, and even higher rates may
be achieved with process optimization. The phosphorus-
35 content of the deposited layer was approximately 5%.

1 The refractive index of the photodeposited phosphorus-doped SiO_2 layer formed as described above was 1.75. The chemical composition of the deposited film was determined by Auger electron spectroscopy to be
5 the value discussed above. The etch rate in "P-etch" [i.e., a mixture of 60 ml of water, 30 ml of 49% HF, and 2 ml of 70% HNO_3] of the phosphorus-doped SiO_2 film was determined to be significantly faster than that
10 of pure SiO_2 , having values comparable to phosphorus-doped films produced by known chemical vapor deposition techniques previously discussed.

 The photochemically deposited phosphorus-doped SiO_2 films formed by the above-described process of the present invention find utility as discussed in relation
15 to Example 2.

 While the present invention has been particularly described with the respect to the preferred embodiments thereof, it will be recognized by those skilled in the art that certain modifications in form and detail may be
20 made without departing from the spirit and scope of the invention. In particular, the scope of the invention is not limited to the photochemical vapor deposition of silicon oxides, but is intended to include the photochemical vapor deposition of an oxide of any gas
25 phase reactant that will react with atomic oxygen, such as reactants containing germanium, gallium, boron, indium, aluminum, titanium, tungsten and hafnium. In addition, the chemically unreactive oxygen-containing precursor is not limited to nitrous oxide, molecular oxygen, or nitrogen
30 dioxide, but is intended to include any material which will photochemically dissociate to atomic oxygen, either with or without mercury sensitization. Further, the substrate on which oxide deposition may be performed by the process of the present invention is not limited to
35 silicon, which was used merely as an example, but may include other semiconductor substrate materials, such as

1 GaAs, HgCdTe, or InSb, or electro-optical materials, such
as lenses or mirrors, or GaAs or Si solar cells. Finally,
the scope of the invention is not limited to the use of
phosphine to produce phosphorus-doping, but is intended
5 to include any dopant-containing precursor which is
capable of mercury photosensitized dissociation to form
neutral particles or which is capable of simultaneous
oxidation by atomic oxygen with the selected gas reactant.
Such precursors include diborane, arsine, stibine, hydrogen
10 selenide, hydrogen sulfide, or hydrogen telluride, to
produce boron-, arsenic-, antimony-, selenium-, sulfur-,
or tellurium-doping, respectively.

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CLAIMS

1. A process for forming a layer of an oxide of a chosen material on the surface of a selected substrate, comprising the steps of exposing the substrate to a vapor-phase reactant and an oxygen-containing precursor in the presence of radiation of a predetermined wavelength to photochemically generate neutral oxygen atoms which react with the vapor-phase reactant to form said oxide layer under selected temperature, pressure and flow rate conditions.
2. A process according to claim 1, wherein said vapor-phase reactant contains silicon, germanium, gallium, boron, indium, aluminum, titanium, tungsten, or hafnium.
3. A process according to claim 2, wherein said vapor-phase reactant is silane (SiH_4) and said oxide is silicon dioxide and/or silicon monoxide.
4. A process according to any preceding claim, wherein said oxygen-containing precursor is nitrous oxide (N_2O), nitrogen dioxide (NO_2), or molecular oxygen (O_2).
5. A process according to any preceding claim, wherein the oxide layer is formed in the presence of photochemically generated dopant atoms to incorporate the dopant atoms into said oxide.
6. A process according to any preceding claim, wherein mercury vapor is added to said reactant and said precursor to cause mercury photosensitized dissociation of a chosen oxygen-containing precursor.
7. A process according to claim 6, wherein the oxygen-containing precursor is nitrous oxide (N_2O), the vapor-phase reactant is silane (SiH_4), the process is performed in a static photochemical reactor whereby the gas ratio of SiH_4 to N_2O is 3 to 12 millimeters, and the temperature at which the process is maintained is 30 to 200°C.

8. A process according to claim 6, wherein the oxygen-containing precursor is nitrous oxide (N_2O), the vapor-phase reactant is silane (SiH_4), the process is performed in a continuous flow photochemical reactor whereby the gas flow ratio of SiH_4 to N_2O is 2 to 10 standard cubic centimeters per minute (sccm), and the temperature at which the process is maintained is 30 to 200°C.

9. A process according to any of the claims 1-5, wherein the oxygen-containing precursor is nitrous oxide (N_2O), the vapor-phase reactant is silane (SiH_4), the predetermined wavelength is 1750 to 1950Å, the gas flow ratio of SiH_4 to ~~oxygen~~ N_2O is 2 to 60 standard cubic centimeters per minute, the temperature at which the process is maintained is 30 to 200°C, and the oxide is silicon dioxide (SiO_2).

10. A process according to any of the claims 1-5, wherein the oxygen-containing precursor is molecular oxygen (O_2) and nitrogen (N_2) is admixed thereto, said predetermined wavelength is 1849Å, the vapor-phase reactant is silane (SiH_4), said pressure is 0 to 5 Torr, and the gas flow ratio of SiH_4 to O_2 to N_2 is 1 to 20 to 80 standard cubic centimeters per minute.

11. A process according to claim 5 or 6, wherein there is provided a dopant-containing precursor which is phosphine (PH_3), diborane (B_2H_6), arsine (AsH_3), stibine (SbH_3), hydrogen selenide (H_2Se), hydrogen sulfide (H_2S), or hydrogen telluride (H_2Te).

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Fig. 1

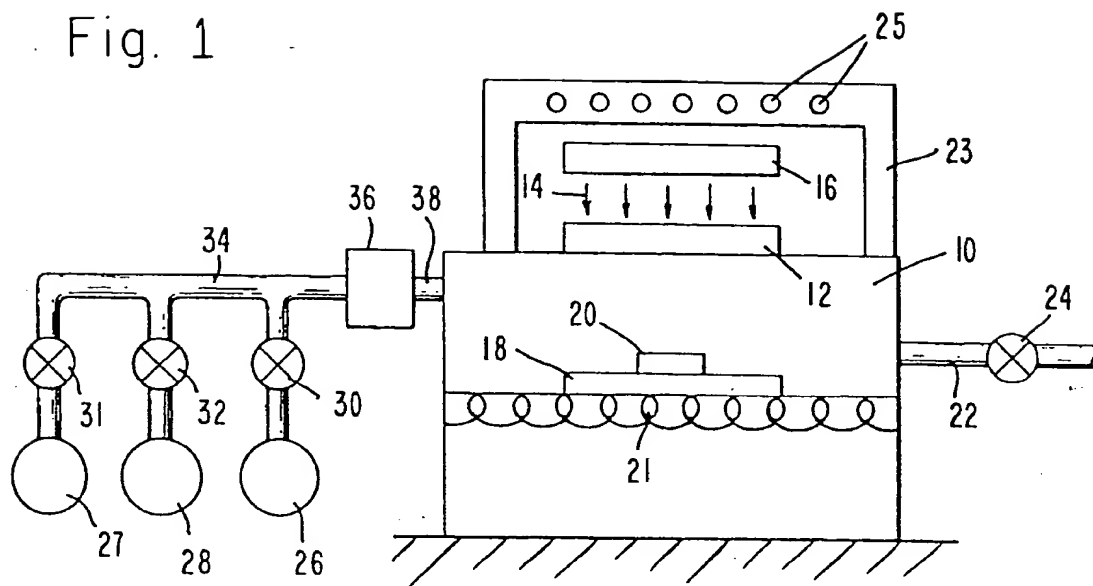
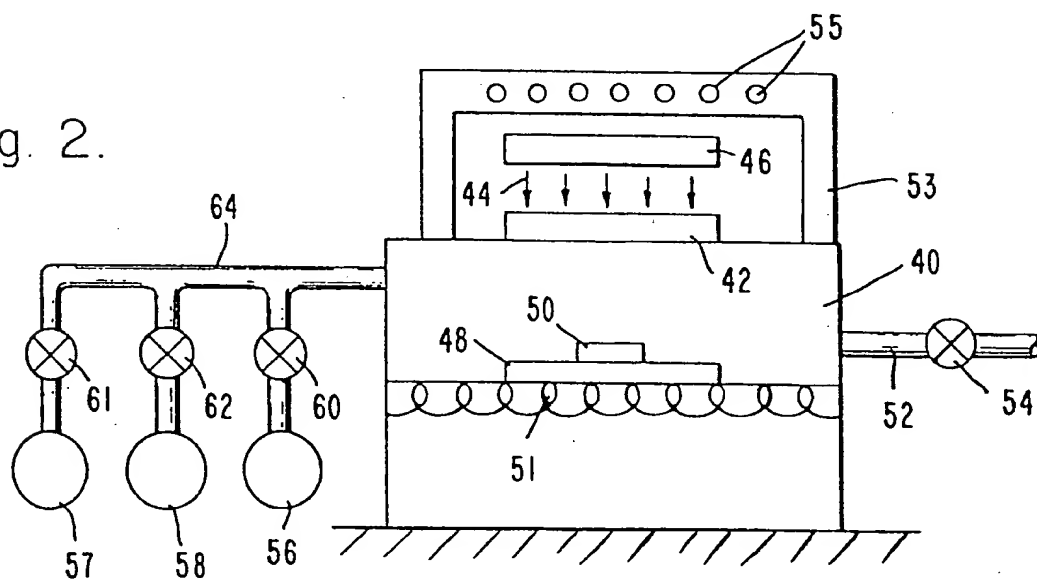


Fig. 2.





European Patent
Office

EUROPEAN SEARCH REPORT

0030798

Application number
EP 80304143.3

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | CLASSIFICATION OF THE APPLICATION (Int. Cl. 1) |
|-------------------------------------|---|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | |
| A | <p>DE - A - 1 564 963 (TEXAS) + Totality + --</p> <p>AT - B - 287 789 (N.V. PHILIPS) + Totality; especially claims 1,2,4,6 + --</p> | | H 01 L 21/205 H 01 L 21/225 H 01 L 21/268/ H 01 L 21/316 H 01 L 21/365 H 01 L 21/385 H 01 L 21/428 |
| A | <p>DE - B - 1 444 520 (RCA) + Totality; especially column 2, line 63 - column 4, line 8; claims 1,2 + --</p> | | TECHNICAL FIELDS SEARCHED (Int. Cl. 1) |
| A | <p>US - A - 3 767 484 (TAKAGI) + Totality; especially column 3, line 68 - column 4, line 3 + --</p> | | B 41 N G 03 F H 01 L |
| A | <p>US - A - 3 907 616 (WIEMER) + Totality; especially column 6, line 49 - column 7, line 10; claims 1,5,7,8 + --</p> | | CATEGORY OF CITED DOCUMENTS |
| D,A | <p>US - A - 3 769 104 (ONO) + Totality; especially column 2, line 67 - column 3, line 21 + --</p> <p>JOURNAL OF VACUUM SCIENCE & TECHNOLOGIE, Vol. 14, No. 5, Sept./Oct. 1977 KERN-ROSIER "Advances in deposition process for passivation films", pages 1082-1099 + Totality + --</p> | | X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons |
| X | The present search report has been drawn up for all claims | | &: member of the same patent family. corresponding document |
| Place of search VIENNA | | Date of completion of the search 19-02-1981 | Examiner FRANZ |



European Patent
Office

EUROPEAN SEARCH REPORT

0030798

Application number

EP 80304143.3

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | CLASSIFICATION OF THE APPLICATION (Int. Cl. ³) |
|-------------------------------------|---|-------------------|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | |
| D, A | JOURNAL OF VACUUM SCIENCE & TECHNOLOGIE, Vol 14, No. 5, Sept./Oct. 1977 AMICK-SCHNABLE-VOSSEN "Deposition techniques for dielectric films on semiconductor devices", pages 1053-1063 + Totality + | | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl. ³) |
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